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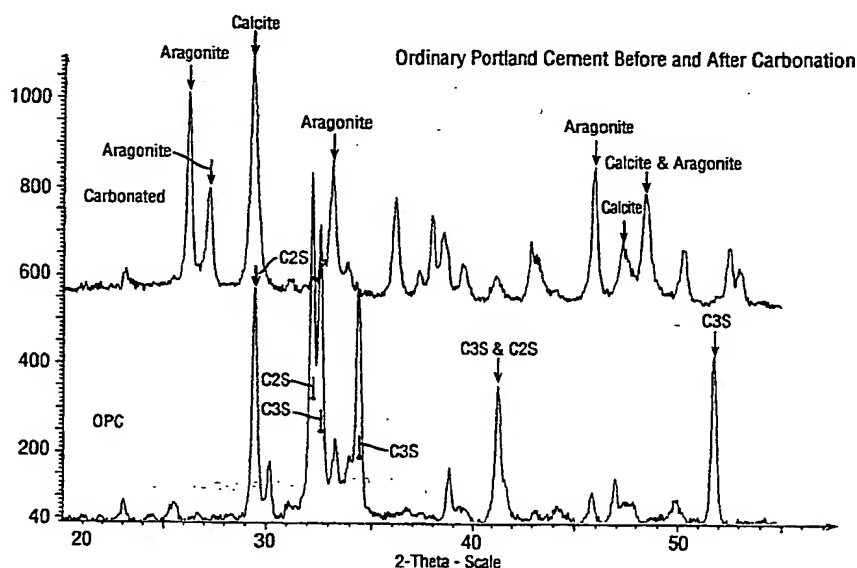
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[Continued on next page]

(54) Title: **SILICATE/ALUMINATE MATERIALS**



(57) Abstract: Silicate-based substantially non hydrated sorbent material comprising predominantly calcium silicate and/or calcium alumino-silicate has an atomic framework at least partially decalcified in that a plurality of calcium atom sites in said atomic framework are vacant. The activated material can be used as industrially useful sorbents for contaminant species such as metal ions, in the solidification of waste, in similar applications, and in the absorption of carbon dioxide which might otherwise be exhausted to atmosphere. The material has a further use as a precipitant of certain ionic species e.g. lead, leading to its removal from aqueous solution by precipitation.

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SILICATE/ALUMINATE MATERIALS

This invention is concerned with silicate and/or aluminate and/or aluminosilicate materials, their preparation and uses. It is more particularly concerned with calcium silicate and/or aluminate materials which have been modified by an 'activation' process
 5 to form a variety of useful sorbents or precipitants.

We have found that calcium silicate-containing materials such as clinkers and glassy residues can be 'activated' by controlled exposure to moisture and carbon dioxide. This may be easily achieved when the clinker is ground or pulverised and dampened. The exposure involves use of a CO₂ medium such as gaseous or other
 10 forms of carbon dioxide or mixtures containing CO₂. It is preferred to expose the material to carbon dioxide immediately upon dampening of the silicate material, to negate any hydraulic or latent activity of the clinker. 'Clinker' is used herein to refer to glassy or crystalline silicate and/or aluminosilicate residues such as, for example, slags, hydraulic cements and latent hydraulic materials and pozzolans within the general
 15 compositional range indicated below. Starting materials for activation can comprise silicate and/or aluminate and/or aluminosilicate having this oxide compositional range. In more preferred starting materials for activation, aluminosilicate species are minimised or avoided. Yet more preferred starting materials may essentially consist of calcium silicate(s) and calcium aluminate(s) having this oxide composition

20	Oxide	% by weight compositional range
	CaO	20 to 95
	SiO ₂	5 to 90
	Al ₂ O ₃	trace to 50
	Fe ₂ O ₃	trace to 35
25	MgO	trace to 20
	Alkalis	trace to 20
	SO ₃	trace to 20
	Others	trace to 35

30 On exposure to carbon dioxide in the presence of a small, preferably carefully controlled amount of water (typically within the water/solids range 0.01 to 0.4), carbon dioxide has been found to become ionised and react with the clinker material. For

example, where the clinker has the following major oxide composition: CaO 65%; SiO₂ 20%; Al₂O₃ 6%; Fe₂O₃ 3% and MgO 1%, then the following reaction products have been found, namely: amorphous silica, polymorphs of calcium carbonate and gibbsite. Other reaction products have been formed depending upon the composition of the clinker.

- 5 Alumino silicate reaction products have been identified in the reaction products of some embodiments, for example where the starting material for activation comprises calcium silicate and aluminate phases. The 'activation' reaction involves a de-calcification reaction that can be effective in minutes even at ambient temperatures and pressures, especially so where fresh anhydrous clinker surfaces are continually exposed to carbon
- 10 dioxide, given appropriate conditions. Other silicate materials may require longer periods for completion of the 'activation' reaction.

The exposure to moisture and CO₂ may be achieved in, for example, a processing step involving milling/crushing/grinding during or subsequent to periods of controlled carbonation.

- 15 During this exposure leading to atomic framework decalcification of the e.g. clinker material, relatively large volumes of carbon dioxide are consumed. The clinker may adsorb quantities of carbon dioxide in excess of 50% of its original dry starting weight. As such, we have found that clinkers and similar calcium silicate/alumino silicate materials have considerable potential to act as carbon dioxide sorbents, whilst
- 20 simultaneously being able to 'imbibe' metallic and other ionic species that may be present (for example) in the carbon dioxide, particularly if the CO₂ gas stream is derived from a waste gaseous discharge. The activated starting materials within the scope of this invention may also or alternatively function as a precipitant e.g. for heavy metals in solution like lead.

- 25 Accordingly, the controlled application of powdered calcium silicate and/or alumino-silicate material such as clinkers to waste or spent gasses containing carbon

dioxide, contaminated with ionic species such as waste metals is one aspect of the present invention.

The silica framework of the activated reaction product preferably has a residual calcium/silicon ratio of less than 1.0, but this may as low as 0.1, or lower or higher than 1.0. This reaction product contrasts with typical starting material calcium/silicon ratio usually between 5 and 1.5. The activated reaction product, apart from containing calcium carbonate unless removed or reacted with said product, is largely amorphous in nature and includes a silica framework, or alumino-silica framework which can be confirmed by x-ray diffractometry as a broad peak with a d-spacing typically of approximately 3 to 4 Angstroms. An additional peak at approximately 7 Angstroms may, or may not, also be present. When the reaction product is dominantly silicious in nature it may approximate to opaline silica in structure. A significant degree of polymerisation can take place during the moisture/CO₂ exposure which can be confirmed by NMR analysis of the framework structure inherent in the 'activated' material.

The framework may have been derived from, in preferred embodiments, a clinker material such as Portland cement. In spite of this, once activated the product remains substantially entirely anhydrous i.e. not hydrated and has a significant sorptive potential. Activated product can be used to treat aqueous waste streams to sorb ionic and possibly non-ionic species as well as treating gaseous waste streams. In addition, the latent sorptive properties of the activated silicate product can be utilised by blending the activated material with contaminated soils or other materials. The activated product also lends itself to application in barrier systems, filter systems and as a pre-solidification adsorbent, for a range of waste streams including radioactive wastes, but not limited to these. The activated product may also be used to treat, or purify, non-waste materials such as in the polishing of potable water or other liquids.

It is preferred that the starting materials for activation are preferably clinkers. The materials preferably contain aluminium, such as aluminium oxide. They may further contain iron.

The carbonation step is preferably carried out at a water solids ratio within the
5 range 0.01 to 2.0; preferably 0.02 to 1.0; more preferably 0.05 to 0.4. The carbonation step is preferably carried out at atmospheric pressure, or up to a pressure not exceeding 30 psi (2 bar). The activated material may be a sorbent or a precipitant for certain species such as lead ions and other heavy metal ions

It is preferred for the surface area of the activated product to be not less than
10 $5\text{m}^2\text{g}^{-1}$. It is especially preferred for the activated product to utilise i.e. react with any carbonate salt produced during the carbonation step. It is also preferred that the starting materials for activation are essentially or entirely polycrystalline in nature, in that they are capable of diffracting X-rays but normally occur as anhydrous products, in other words not as well defined crystals with parallel sides and defined axes ratios. In the
15 activated product, it is preferred that the only significant mineral crystalline phases are calcite and aragonite. These are polymorphs of anhydrous CaCO_3 . Alumino silicate crystalline starting material, which is preferred, has 4-co-ordinate (tetrahedral) and 6-co-ordinate (octahedral) Aluminium species present. It is preferred for the carbonated (activated) such material only to comprise 4-co-ordinate Aluminium species, and which is
20 distinct structurally from the original 4-co-ordinate Al atoms. It appears that most of the Al thereby present is available for reaction.

It is most preferred for the starting material for activation to be an anhydrous polycrystalline material predominantly composed of one or more calcium silicates and/or calcium aluminates. Such polycrystalline material preferably essentially consists of
25 calcium silicates and/or calcium aluminates material.

The activated material can combine with CO_2 in the presence of moisture, at ambient temperature and pressure. It is not usually necessary or desirable to employ heating or cooling when using the activated product, to sorb CO_2 .

It is preferred that the activated material after use to sorb CO_2 does not retain
5 hydraulic properties, and furthermore such product after use is preferably still essentially non-hydrated. The reacted such product cannot therefore be used as a cement material.

It is especially preferred for the reaction product to comprise a Q^4 amorphous silicate network in which all the Al species have become tetrahedral.

Accelerated carbonation providing the activation of the silica framework
10 apparently imparts physical modifications to the surface of such 'activated' grains. Although surface area of the activated materials remains relatively low, atomic sized holes, preferably funnel-shaped, and typically within the size range 1 to 100 Angstroms are formed in the surface of individual grains. These holes form channels or pathways into the interior of individual grains and facilitate the sorption of other species such as the
15 contaminants just described into the activated medium. The channels can have unusual shapes e.g. as funnels or wedges, which further enhances retention of such contaminant species within or upon the grains of activated product. In addition, by varying the chemical and physical nature of the calcium silicate and/or calcium aluminate starting material and/or the accelerated carbonation processing environment, the size and shape
20 of such channels can be varied. In this way micro-and meso-porous materials can be engineered.

The application of decalcified, 'activated' silicate materials (such as clinker) in the treatment of aqueous solutions, non-aqueous solutions, gasses and solids, such as, for example, as a sorbent with latent potential in the treatment of e.g. contaminated land
25 and as barrier, filter and purifying system represents a second aspect of this invention.

The present calcium silicate and/or calcium aluminate adsorbents can be produced at ordinary temperatures and pressures. However, elevated or lowered

pressures and temperatures may also be used depending on the chemistry of the silicate and the type of carbon dioxide utilised. For example, where supercritical carbon dioxide is selected, the temperature regime will preferably vary between 30 and 100°C and the pressure between 50 and 180 bar.

5 The clinkers that are preferred for activation have a silicate phase mineralogy dominated by di-calcium silicate (C_2S) and tri-calcium silicate (C_3S). However, they may also be composed of calcium silicates and/or calcium aluminates. Typical oxide analyses of these preferred clinkers show CaO contents of between 50% to 95%, SiO_2 content of 10 to 50%, and Al_2O_3 content of between 0% and 15%.

10 Subsequently to use as a sorbent or precipitant and even when the 'activated' silicate is apparently spent, the used product may undergo re-calcination in a kiln followed by re-carbonation to reactivate the apparently spent material. Therefore, even when used for a first time and thus apparently spent, the material containing sorbed waste species can have potential for re-activation and re-use, even more than once.

15 Hence recycling of used material is contemplated. The incorporation of metallic species in particular into re-calcined clinker surprisingly seems to improve its subsequent sorptive potential upon re-activation by accelerated carbonation.

 Although water, in low or trace amounts, is introduced during the activation step with CO_2 , it is particularly preferred for there to be substantially no residual water

20 associated with or hydrating the silica framework lattice of the activated product.

 In order that the invention may be further appreciated, the following non-limiting examples are presented. Reference is also made to the accompanying drawings in which:

 Figure 1 is an X-ray diffractogram showing the phases present in ordinary

25 Portland Cement before and after carbonation, and

Figure 2 is an example of cadmium removal using an activated product of this invention based on OPC and compared with CaCO_3 . It illustrates that in this embodiment, removal of Cd is by sorption and not precipitation.

Example 1

5 A prepared, de-calcified, activated Portland cement clinker with the following approximate composition: CaO 65%, SiO_2 20%, Al_2O_3 5%, Fe_2O_3 5%, MgO 1.5%, Alkalis, 0.7%, SO_3 , 1.5% and LOI 1.3%, was assessed for its ability to sorb metals (i.e. metallic ions) from aqueous solution. A typical X-ray diffractogramme before and after carbonation is given in Figure 1.

10 Fig. 1 shows XRD data for powdered specimens of carbonated OPC (top) and OPC. The identifiable crystalline phases of carbonated OPC are Aragonite and Calcite (polymorphs of calcium carbonate). The identifiable crystalline phases of OPC are di- and tri - calcium silicate. Hence, after carbonation essentially all of the di- and tri - calcium silicate have reacted.

15 A number of metal nitrate solutions were prepared with a concentration of 1000mg metal/l. The metals chosen were copper, zinc, nickel and chromium. The solution exposed to the sorbent was sampled at intervals up to 69 hours. The amount of metals removed by the sorbent during this experiment was used to assess the sorptive capacity of the novel material.

20 0.5g of sorbent was placed in an acid washed 250ml container followed by 100 ml of each metal solution taken from a pre-prepared stock solution. All samples were prepared in triplicate from double distilled water together with control solutions containing metals without sorbent and water (blank solution) without sorbent. All the metal solutions were taken from a standard metal solution. Sample solutions were placed in a
25 shaker at a constant temperature of 20°C. Table 1 gives the number of samples examined in this experiment.

Table 1 : Number of samples

Metal solution + sorbent	15
Distilled water + sorbent	3
Metal solution only	15
Distilled water only	3

5 Solutions were sampled at zero time, 15 minutes, 3, 14, 18, 21, 45 and 69 hours. Containers were centrifuged prior to extraction of 10ml of solution. Each 10ml sample was measured for pH and then acidified with 100 μ l Aristar HNO₃ prior to analysis by AAS.

 At the end of the example the solutions containing sorbent were centrifuged for 30
10 min. The remaining solution was decanted into a 100ml container and acidified with 300 μ l of Aristar HNO₃. The sorbent residue left in the 250ml container was oven dried at 55°C prior to further examination.

Analysis of sample solutions

 Acidified single metal solutions and one multi-element solution containing all the 5
15 metals were prepared from a certified standard solution with the concentration 1.000 mg/l prior to analysis by AAS (PYE Unicam SP9 AAS).

 The results are summarised in table 2. The difference in measured starting solution from those predicted was due to the vastly different water of crystallisation in the metal nitrate salts from that described by the reagent's manufacturer.

20 The concentrations of metals in solution in contact with the sorbent decreased steadily with time, however for Cu and Ni solutions equilibrium was not reached although given more time, it would be expected that more of these metals should be removable from solution.

Table 2: Summary of results obtained

Metal	Mean metal Concentration (zero time)	Mean metal concentration (15 mins.)	Mean metal concentration (69 hrs.)	Sorption in Mmol. Metal/ g sorbent at 69 hrs.	% decrease
Cu	856	791	465	12.3	46 %
Ni	752	800	623	4.39	17 %
Cr	336	189	20.6	12.1	94 %
Pb	765	221	53.7	6.87	93 %
Zn	867	708	19.5	25.9	98 %

Example 2

A commercially available cementitious clinker was prepared. The approximate
 5 Bogue composition was: C_3S 51%, C_2S 25%, C_3A 11%, C_4AF 1%, SO_3 2.6%, and alkalis
 of 0.25%.

The dry clinker was placed in a steel carbonation chamber immediately after the
 addition of water. The water/solids ratio used was 0.1. The chamber was purged of air
 and CO_2 gas was introduced at a pressure of 2bar. Immediately the pressure was seen
 10 to drop as CO_2 gas was consumed. After approximately 1 hour, the sample was
 removed and dried in an oven for a further hour at 105°C. The dry material was then
 weighed and ground to expose fresh silica surfaces in a mortar and pestle. Five cycles
 of wetting followed by carbonation and grinding were necessary to completely carbonate
 the clinker.

15 Complete carbonation was identified by x-ray diffractometry when the original
 anhydrous clinker phases, including C_3S , were no longer identifiable. During this
 example the mass of the clinker was found to increase by in excess of 50% of its initial
 dry weight. This mass increase was due to the amount of CO_2 that had been adsorbed
 during the accelerated carbonation step.

20 X-ray diffractometry revealed a large diffraction pattern relating to the formation
 of calcium carbonate and broad peaks at approximately 23°C 2-theta and 12°2-theta.

Preferred embodiments of the first aspect of the invention are based on the
 controlled exposure of ground clinker to a gaseous waste stream containing CO_2 and

one or more contaminant species so that the activated clinker adsorbs considerable quantities of both gaseous CO_2 and such contaminants.

Preferred embodiments of the second aspect of the present invention are based on the controlled application of accelerated carbonation in order to de-calcify and hence
5 activate the clinker to a state (calcium vacancies in framework) wherein it has latent sorptive properties. On subsequent exposure to aqueous and non-aqueous solutions, or on exposure to other waste streams, the activated clinker then acts as an industrially useful adsorbent.

Further examples of the invention, examples 1a to 14 inclusive are presented
10 overleaf.

With reference to Figures 2 and 3: 1g of carbonated sorbent was added to 200ml of cadmium nitrate solution at an initial concentration of 1000ppm with respect to cadmium. Plot Cd/CC/N (Fig. 2) indicates the change in concentration of cadmium as a function of time. After 72 hours essentially all of the cadmium has been removed from
15 solution. A similar investigation in which 1g of calcium carbonate was added to 200ml of 1000ppm cadmium nitrate (plot Cd/ CaCO_3 /N, Fig. 2) indicates that the presence of calcium carbonate does not result in the precipitation and exclusion from solution of cadmium species. Plot Cd/N shows the concentration of cadmium in a control specimen to which there were no solid additions. Hence, the mechanism of exclusion of cadmium
20 from the solution is by sorption to the aluminosilicate matrix of the carbonated sorbent. Fig. 3 indicates that the pH range of all specimens are similar.

The starting materials can be easily obtained at low cost. The process requires only the use of CO_2 thereby producing no or minimal waste. The invention is environmentally beneficial, both in its manufacture and its use. Modification of the
25 materials and/or reaction conditions in the making of the sorbent may modify its pore structure. It has been found particularly beneficial for the activated product to incorporate funnel-shaped pores. Thus, varying reaction conditions using gaseous or

super critical CO₂ provides for changes in the microcrystallinity and microporosity that can have a beneficial impact on sorbent characteristics such as sorption capacity and re-calcination potential.

One of the advantages of the activated material is that it has widespread
5 industrial application, for example in gas stacks as a CO₂ absorber, in waste effluent plumes to remove metal contaminants, in water treatment systems and in remediating contaminated land.

Compared to other known sorbents, embodiments of the presently provided
activated material can be produced economically and even more so by using recycled
10 CO₂ discharged during cement making or other processes with the simultaneous environmental benefits of reducing greenhouse gas emissions.

Sample Summary of Chemistry, Mineralogy and Percentage Carbon Dioxide Uplake												
Ex	Sample Source	Sample bulk Chemistry					Other components			Dominant Mineralogy	CO ₂ uplake (% weight gain)	
		CaO	SiO ₂	MgO	Fe ₂ O ₃	Al ₂ O ₃	LOI	wt %	constituents			
1a	Ordinary Portland cement	65.04	20.71	1.03	2.77	4.83	1.26	4.36		C ₂ S, C ₃ S	22.3	
2a	Stainless steel slag	46.66	27.92	9.75	1.22	2.91	4.28	7.26	Chromium, Fluorine	C ₂ S, Merwinite Akermanite	20.3	
3	Ash from combustion of de-inking sludge from paper recycling	37.69	33.76	3.72	0.03	20.12	1.16	3.52		Gehlenite, Anorthite, C ₂ S	16.8	
4	Pulverised Fuel Ash	3.36	46.96	1.76	11.33	23.71	5.66	7.22		Amorphous, + Small % Quartz	1.2	
5	Ground Granulated Blastfurnance Slag	41.38	34.59	6.84	1.51	14.02	0.00	1.66		Amorphous	2.8	
6	Municipal Solid Waste Incineration Ash	35.89	15.29	1.29	1.11	6.25	26.23	13.94	Chlorine, Sodium, Potassium, Sulphate	NaCl, KCl, CaSO4	14.0	
7	Municipal Solid Waste Incineration Ash	22.62	10.32	1.61	0.95	5.30	34.42	24.78	Chlorine, Sodium, Potassium, Sulphate	NaCl, KCl, CaSO4	6.5	
8	Precipitated calcium silicate powder	56.00	44.00							Amorphous	9.0	
Materials below have approximate bulk chemistry												
9	Cupola Arrester filter cake	8	15	2	23	4	0	49	~32% Zn from perchloric acid digest	Zn oxides, Magnetite	7.5	
10	Steel Slag	46	10	3	1	32	0	9		Fluorite, Akermanite, Gehlenite	2.7	
11	Steel Slag	11	40	35	1	8	0	6		Olivine, Quartz, Magnetite	0.6	
12	Cyclone Dust	6	30	1	39	6	17	2		Un identified	2.4	
13	Cupola Furnance Dust	25	30	1	23	4	0	18		Amorphous	3.7	
14	Slag	37	41	2	1	12	0	9			0.6	

CLAIMS

- 1) Silicate-based substantially unhydrated sorbent material comprising at least one calcium silicate and/or at least one calcium aluminate and/or at least one calcium alumino-silicate of which the atomic framework is at least partially decalcified in that a plurality of calcium atom sites in said atomic framework are vacant.
- 2) Material as claimed in claim 1 mainly or substantially comprising said silicate and/or aluminate.
- 3) Material as claimed in either preceding claim which is a calcium-silicate based clinker, glassy residue, slag, pozzolanic material, hydraulic cement or latent hydraulic material.
- 4) Material as claimed in any preceding claim which is ground or pulverised.
- 5) Material as claimed in any preceding claim which is anhydrous.
- 6) Material as claimed in any one of claims 1 to 4 containing at least a trace amount of moisture.
- 7) Material as claimed in claim 6 in which the water to solids ratio is from 0.001 to 10.00, preferably 0.005 to 5.0, more preferably 0.0005 to 1.0, most preferably 0.01 to 0.5.
- 8) Material as claimed in any one of claims 1 to 7 which satisfies the following compositional range in terms of % by weight
- | | | | | | |
|------------------|----------|------------|----------|-----------------|----------|
| CaO | 20 - 95% | preferably | 30 - 95% | more preferably | 55 - 95% |
| SiO ₂ | 5 - 90% | preferably | 10 - 80% | more preferably | 10 - 50% |

	Al ₂ O ₃	trace - 50%	preferably	trace - 40%	more preferably	0 - 15%
	Fe ₂ O ₃	trace - 35%	preferably	trace - 25%	more preferably	0 - 10%
	MgO	trace - 20%	preferably	trace - 10%	more preferably	0 - 5%
	Alkalis	trace - 20%	preferably	trace - 10%	more preferably	0 - 2%
5	SO ₃	trace - 20%	preferably	trace - 10%	more preferably	0 - 2%
	Others	trace - 35%	preferably	trace - 25%	more preferably	0 - 5%

- 9) Material as claimed in any preceding claim which is at least partly polymerised.
- 10) Material as claimed in any preceding claim which has been caused or allowed to react with other material containing a sorptive species such as ionic species capable of retention in or by the said vacant calcium sites in the atomic framework of the silicate and/or calcium aluminate.
- 11) Material as claimed in claim 10 in which the said other material is selected from : waste gas stream, solid waste, contaminated soil, metallic compounds, ionic compounds, radioactive waste.
- 12) A method of making a material as claimed in any one of claims 1 to 9 from a starting material containing said calcium silicate and/or aluminate and/or aluminosilicate which comprises applying at least a trace amount of moisture to said material followed by exposure of the moistened material to a medium which predominantly contains carbon dioxide.
- 13) A method as claimed in claim 12 in which the medium essentially consists of carbon dioxide apart from unavoidable impurities, such as pressurised carbon dioxide gas or supercritical carbon dioxide liquid or solid carbon dioxide.
- 14) A method as claimed in claim 12 in which the medium is a gaseous atmosphere derived from a waste gas stream containing not only carbon dioxide but also one or

more waste species intended to be absorbed by or adsorbed onto the said material as claimed in any one of claims 1 to 11.

15) A method as claimed in any one of claims 12 to 14 in which the medium is a
5 gaseous atmosphere which is pressurised and/or the exposure is carried out at an elevated temperature.

16) A method as claimed in claim 15 in which the exposure is carried out in a pressurised reactor which is evacuated prior to charging with carbon dioxide or a
10 gaseous mixture predominantly of carbon dioxide.

17) A method as claimed in any one of claims 12 to 16 as applied to the production of a material as claimed in any one of claims 2 to 9.

15 18) A method as claimed in any one of claims 12 to 17 operated more than once as a batch process, wherein during or between at least one successive exposure to the said medium, the starting material is further ground or pulverised or milled to expose additional surface of the material for said exposure.

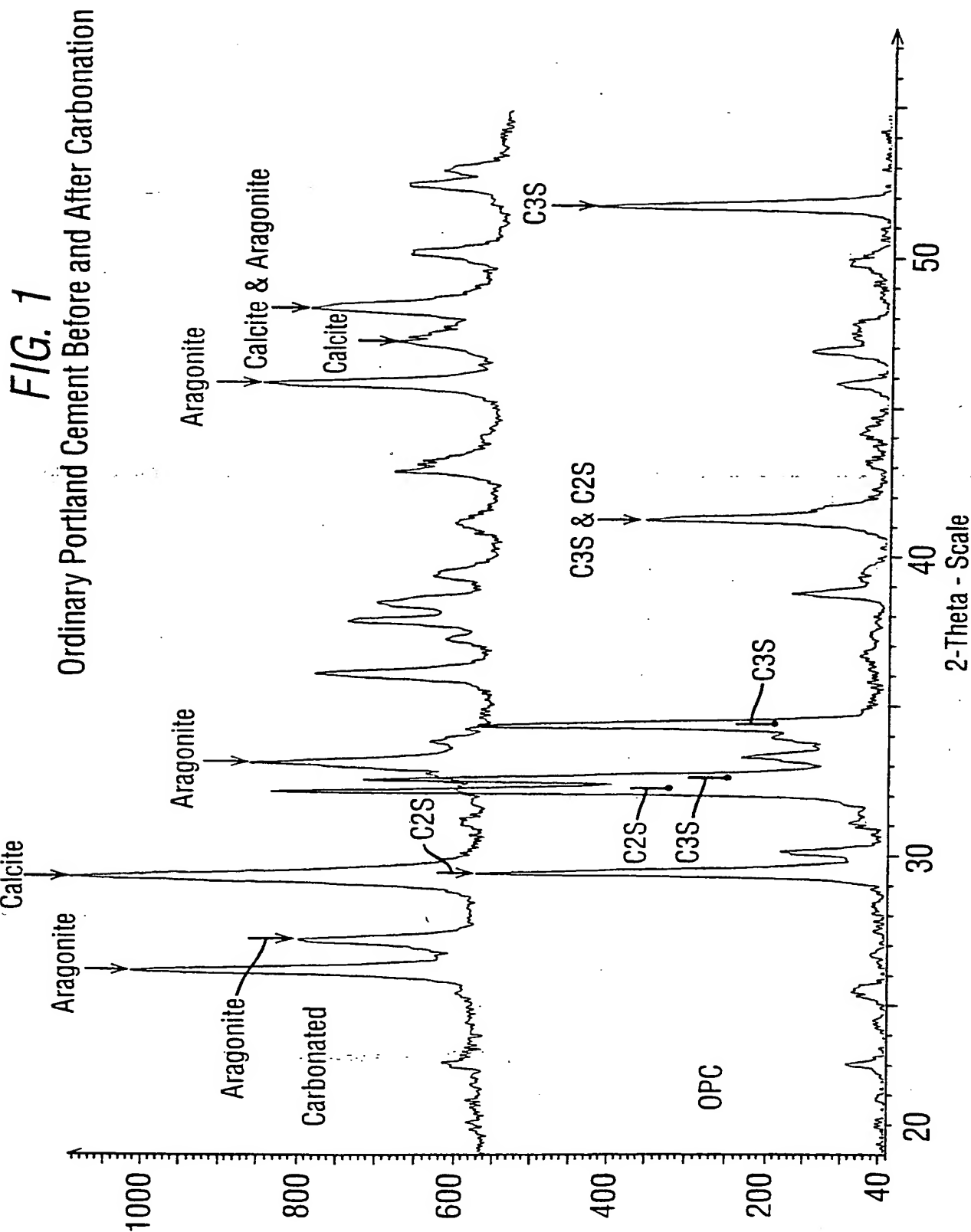
20 19) Use of a material as claimed in any one of claims 1 to 9 in the treatment of other material containing at least one sorptive species as defined in claim 9, to produce solidified reaction product for disposal or other processing.

20) Use of solidified reaction product as defined in claim 19 as the starting material in
25 a method of making a material as defined in any one of claims 12 to 18.

21) Use of a material as claimed in any one of claims 1 to 9 as a precipitant of metal ions from solution.

22) Use as claimed in claim 21 in which said metal ions are lead ions.

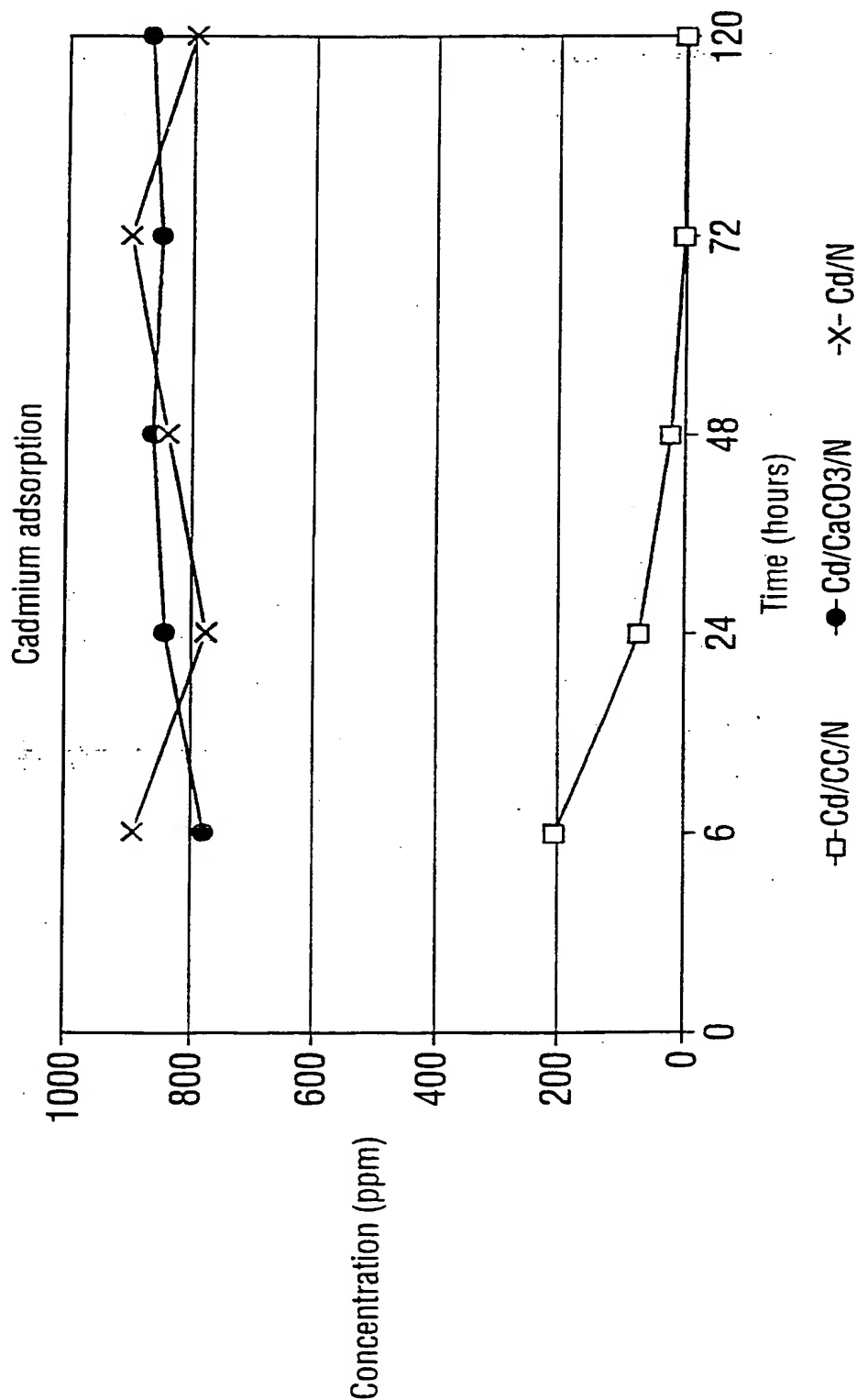
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FIG. 2

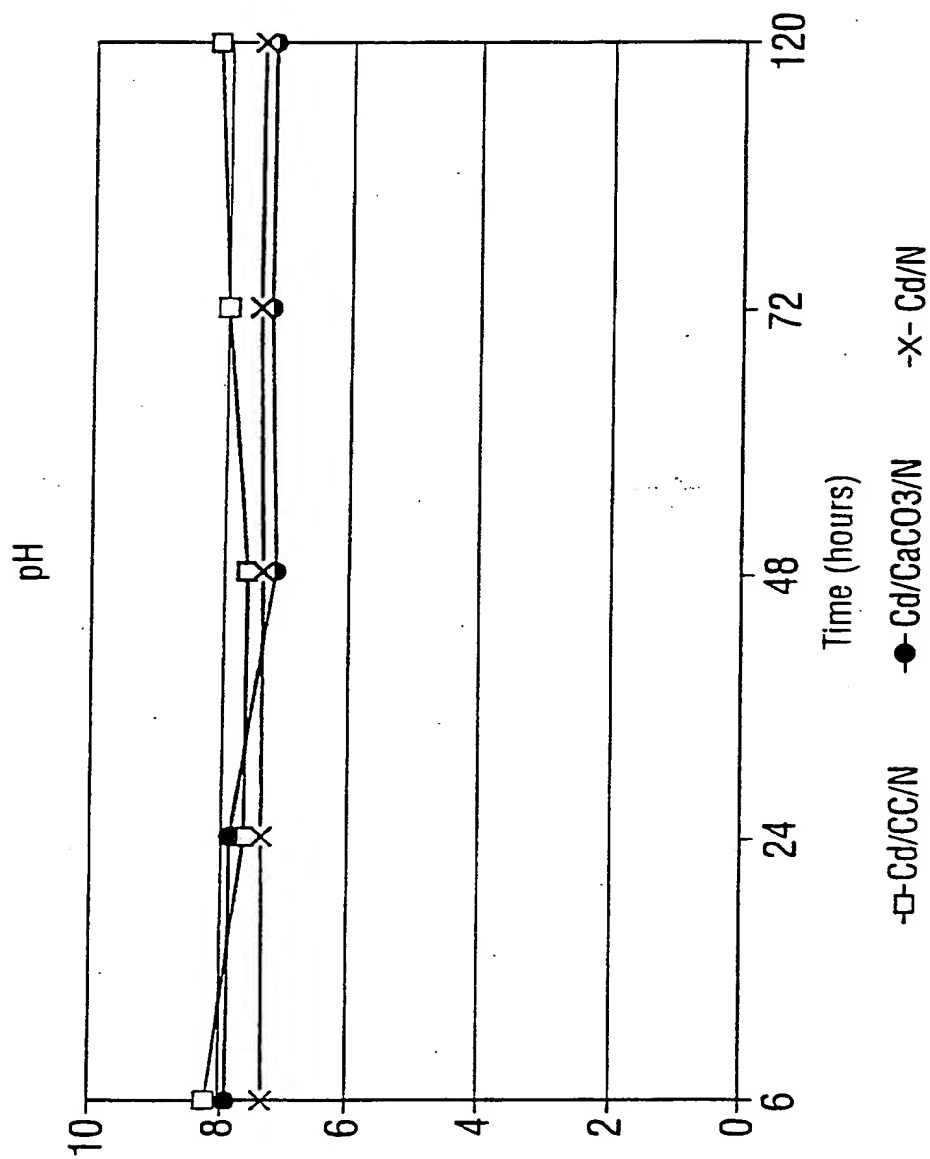


Abbreviations:

Cd/CC/N - cadmium solution mixed with carbonated cement (5g/l) under natural pH;
 Cd/CaCO3/N - cadmium solution mixed with calcium carbonate (reference material (5g/l)) under natural pH;
 Cd/N - cadmium solution without sorbent under natural pH;

3/3

FIG. 3



Abbreviations:

Cd/CC/N - cadmium solution mixed with carbonated cement (5g/l) under natural pH;

Cd/CaCO₃/N - cadmium solution mixed with calcium carbonate (reference material (5g/l)) under natural pH;

Cd/N - cadmium solution without sorbent under natural pH;

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J20/10 B01J20/16 C02F1/52 //C02F101/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, INSPEC, COMPENDEX, CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

7 March 2001

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

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